Mechanisms of Decoherence in Weakly Anisotropic Molecular Magnets

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Decoherence mechanisms in crystals of weakly anisotropic magnetic molecules, such as V_{15}, are studied. We show that an important decohering factor is the rapid thermal fluctuation of dipolar interactions between magnetic molecules. A model is proposed to describe the influence of this source of decoherence. Based on the exact solution of this model, we show that at relatively high temperatures, about 0.5 K, the quantum coherence in a V_{15} molecule is not suppressed and, in principle, can be detected experimentally. Therefore, these molecules may be suitable prototype systems for study of physical processes taking place in quantum computers.

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A new class of magnetic compounds, molecular magnets [1], has been attracting much attention. Each molecule of such a compound is a nanomagnetic entity with a large spin (or, in the antiferromagnet case, large staggered magnetization). The interaction between different molecules, being of the dipole-dipole type, is very small, so that the corresponding crystal is an arrangement of identical weakly interacting nanomagnets. Molecular magnets are ideal objects to study phenomena of great scientific importance for mesoscopic physics, such as spin relaxation in nanomagnets, quantum tunneling of magnetization, topological quantum phase interference, quantum coherence, etc. [2]. Low-spin weakly anisotropic compounds, like V_{15} [3,4], demonstrate well-pronounced quantum properties, such as significant tunneling splitting of low-lying spin states. As we show here, they are attractive prototype systems to study mesoscopic quantum coherence and physical processes which destroy it. Besides fundamental science, these studies are important also for the implementation of quantum computation [5].

At present, for strongly anisotropic high-spin magnetic molecules such as Mn_{12} and Fe_8, different kinds of decohering interactions have been studied [6,7] and their interplay with quantum properties at low temperatures (below 1.5–2 K) is well understood. A general conclusion [7] about strongly anisotropic systems is that the dissipative environment, especially the bath of nuclear spins, rapidly destroys coherence even at very low temperatures, and only incoherent tunneling survives.

Decoherence in weakly anisotropic magnetic molecules has not yet received much study, but such a study is the main purpose of the present paper. We analyze various sources of decoherence for such molecular magnets as V_{15} and show that in the temperature range 0.2–0.5 K the decoherence is governed by rapidly fluctuating dipole-dipole fields produced by thermally activated molecules. This mechanism in molecular magnets has not been considered before; estimates show that in strongly anisotropic magnets like Mn_{12} or Fe_8 this effect is small. Based on an exactly solvable model, we demonstrate that even at temperatures as high as 0.5 K, the quantum coherence in V_{15} molecules is remarkably robust, and, in principle, can be detected experimentally. Therefore, the V_{15} molecular magnet is a promising candidate for the study of quantum coherence and may be a useful prototype system for the investigation of physical processes taking place in quantum computers.

The magnetic subsystem of the molecule $K_6[V_{15}As_6O_{42}(H_2O)] \cdot 8H_2O$ (denoted for brevity as V_{15}) consists of fifteen V^{4+} ions with the spin $1/2$ (see Fig. 1). The ions form two nonplanar hexagons (with total spin equal to zero) and a triangle sandwiched between them. Exchange interactions between ions are reasonably large (from 30 to 800 K), but, due to the strong spin frustration present in the molecule, the couplings of the central triangle spins with the hexagons cancel each other (see Fig. 1). The hexagon spins form a rather stiff antiferromagnetic structure, and the low-energy part of the spectrum is defined by only three weakly coupled spin $1/2$ ions belonging to the central triangle. An effective exchange coupling between the triangle spins $J \simeq 2.5$ K is present. Thus, the ground-state term consisting of two doublets with $S = 1/2$ is separated from the low-lying excited term $S = 3/2$

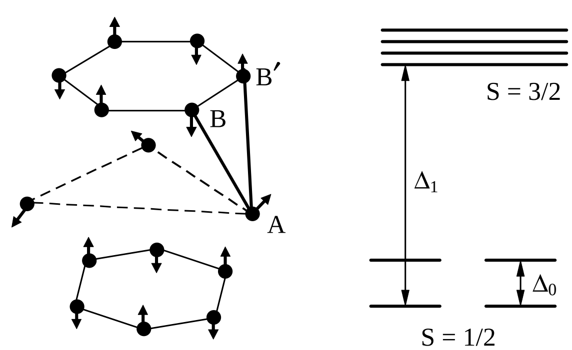

FIG. 1. Sketch of the V_{15} molecule. The spins B and B' of the upper hexagon form a very stiff antiferromagnetic dimer: $J_{BB'} \sim 800$ K. The spin A from the central triangle is coupled antiferromagnetically to both B and B', so J_{AB} and $J_{AB'}$ cancel each other to a large extent ($J_{AB}, J_{AB'} \ll J_{BB'}$). This frustration effectively decouples the triangle spins from the hexagons. Because of C_{3v} symmetry of the molecule, the situation is the same for all the triangle spins.

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by the distance $\Delta_1 = 3J/2 \simeq 3.8$ K. Experimental results [4] suggest that within the two ground-state doublets, the states $|S = 1/2, S_z = +1/2\rangle$ and $|S = 1/2, S_z = -1/2\rangle$ are mixed (a small anisotropic interaction may be responsible, but it is not of concern for the arguments presented), so that tunneling between these levels occurs and the fourfold degeneracy of the ground state is partly lifted (it cannot be lifted completely because of Kramers' theorem: in the absence of an external field all levels are doubly degenerate). The coherent tunneling leads to a splitting $\Delta_0 \simeq 0.2$ K [4] between the two pairs of Kramers-degenerate levels. The aim of this paper is to study the decoherent influence of the environment upon this tunneling, i.e., the decoherence between the states $|S = 1/2, S_z = +1/2\rangle$ and $|S = 1/2, S_z = -1/2\rangle$.

First, we consider decoherence caused by the spin-lattice relaxation. The rate of the relaxation due to direct one-phonon processes can be estimated [8,9] as

$$(\tau_{\rm sl}^{\rm dir})^{-1} = 9\pi \frac{|V_{\rm sl}|^2}{Mv^2}\left(\frac{\Delta_0}{\theta}\right)^3 \coth\left(\frac{\Delta_0}{2T}\right), \tag{1}$$

where Δ_0 is the tunneling splitting of the ground-state doublets, T is the temperature, $v \approx 2800$ m/s [4] is the sound velocity in the molecular crystal, $M \approx 2.3 \times 10^3$ amu is the mass of the molecule, $\theta = (6\pi^2 v^3/\Omega_0)^{1/3} \simeq 70$ K is the Debye temperature (Ω_0 is the volume per molecule), and $V_{\rm sl}$ is the characteristic "modulation" of spin energy under long-wavelength acoustic deformation. At present, the physical mechanism of spin-lattice coupling is unclear, but the value of $V_{\rm sl} \simeq 2.6$ K has been estimated from the available experimental data [4]. As a result, the estimate is $(\tau_{\rm sl}^{\rm dir})^{-1} \simeq 2T \times 10^{-11}$ K (where T is the temperature in kelvins). Here and below, we put $\hbar = k_B = 1$ and express all quantities, including relaxation time, in the same units (kelvins). Also, there is a contribution from Raman two-phonon processes, but at low temperatures the corresponding relaxation time $\tau_{\rm sl}^R$ is very long: $\tau_{\rm sl}^{\rm dir}/\tau_{\rm sl}^R \simeq T^6/(Mv^2\Delta_0^2\theta^3) \ll 1$ [8,9] and can be neglected.

We also consider Orbach two-step relaxation via the excited levels $S = 3/2$ [9] (see Fig. 1):

$$(\tau_{\rm sl}^{\rm Or})^{-1} = 9\pi \frac{|V_{\rm sl}|^2}{Mv^2}\left(\frac{\Delta_1}{\theta}\right)^3 \exp\left(-\frac{\Delta_1}{T}\right) \tag{2}$$

and for the parameters of V_{15} we have $(\tau_{\rm sl}^{\rm Or})^{-1} \simeq 10^{-8}\exp(-\Delta_1/T)$ K. Here, we assume that the spin-lattice matrix element $V_{\rm sl}$ is of the same order as above (about 2.6 K).

Along with triggering Orbach processes, the excitation of molecules to the level $S = 3/2$ leads to a variation of the dipolar field exerted on a given molecule. As time goes by, some of the excited molecules relax back to $S = 1/2$, while other molecules go up to the level $S = 3/2$, and the dipolar field at a given point in the crystal fluctuates with time. In this paper, we use a mean-field approach to take into account the dipolar fields acting on molecules; it is justified since we are dealing with the case of relatively high temperatures (in comparison with the energy of dipolar interactions Γ_0) and long-range dipolar forces. Within the mean-field approach, the dipolar field of the molecule with the spin $\mathbf{S}_2$ (equal to 3/2) can be imagined as a sum of the field created by a spin $\mathbf{S}_1$ (equal to 1/2) and a field created by the spin $\mathbf{S}' = \mathbf{S}_2 - \mathbf{S}_1$. Thus, the total dipolar field is a sum of two fields: the static demagnetizing field created by a uniform medium of spins 1/2, and a purely fluctuating field h created by the spins $\mathbf{S}'$. The spins $\mathbf{S}'$ are distributed approximately uniformly over the sample at any instant, and their number N_1 is small in comparison with the total number N of molecules, $N_1 = N\exp(-\Delta_1/T)$, so the fluctuating field h at any instant obeys the Cauchy (Lorentz) distribution (Chap. IV, Ref. [8]):

$$P(h) = \frac{\Gamma}{\pi}\frac{1}{h^2 + \Gamma^2} \tag{3}$$

with $\Gamma = \Gamma_0(N_1/N) = \Gamma_0\exp(-\Delta_1/T)$, where $\Gamma_0 \simeq 10^{-4}$ K is of order of the dipole-dipole interaction energy in the ground state. Note that the fluctuating field h is measured against the total static field, including the static dipolar field. A comparison with Eqs. (1) and (2) shows that at $T > 0.2$ K the distribution width Γ is much larger than $1/\tau_{\rm sl}$, so that the fluctuating field h destroys coherence much faster than phonons do. Therefore, the fluctuating dipole-dipole field constitutes an important decoherence factor.

To estimate the correlation time of the dipolar field fluctuations, we note that the field changes when excited molecules relax back to the $S = 1/2$ level (and, according to the principle of detailed balance, the same number of molecules go to the level $S = 3/2$). The transition from $S = 3/2$ to $S = 1/2$ proceeds via emission of phonons of energy Δ_1. The rate of this transition is proportional to Δ_1^3 (the number of phonons with energy Δ_1) and can be calculated using the Fermi's golden rule (Chap. 10, Ref. [9]):

$$\tau_c^{-1} = 9\pi \frac{|V_{\rm sl}|^2}{Mv^2}\left(\frac{\Delta_1}{\theta}\right)^3, \tag{4}$$

which satisfies the condition of detailed balance between the levels $S = 3/2$ to $S = 1/2$ [cf. Eqs. (4) and (2), representing the rates of transitions "up" and "down"), so the level populations remain constant in time. During the time τ_c, a majority of the molecules situated initially in the state $S = 3/2$ relax to $S = 1/2$, and other molecules are excited, causing the field to fluctuate. Thus, τ_c is the correlation time for the fluctuating dipolar field. The estimate gives $\tau_c^{-1} \simeq 10^{-8}$ K for V_{15}, so that $\Gamma\tau_c \ll 1$ at $T < 0.5$ K; i.e., the field fluctuations are fast in comparison with their amplitude.

Now, let us consider the hyperfine fields which constitute an important source of decoherence [7]. A typical time for fluctuations of the hyperfine field τ_n is of order of the linewidth of nuclear magnetic resonance and can be estimated as dipole-dipole interactions between different nuclei [8]: $1/\tau_n \sim (\mu_n/\mu_e)^2\Gamma_0$, where μ_n, μ_e are nuclear and electronic magnetic moments, respectively. Therefore, for the temperatures $T > \Delta_1/[2\ln(\mu_n/\mu_e)] \simeq 0.2$ K one has $\tau_n\Gamma \gg 1$ and hyperfine fields can be considered as static for time intervals of order Γ^{-1}. As will be shown below, Γ defines the relaxation (decoherence) time, so that hyperfine fields can be combined with static demagnetizing fields to give some total static mean-field bias h_0 of the doublet levels. This bias is determined mainly by the hyperfine field exerted on a molecule, which is about $\Gamma_{hf} \simeq 5 \times 10^{-2}$ K [4] (demagnetizing fields are weaker), and is of order of the tunneling splitting Δ_0. Therefore, for a large fraction of the molecules the levels $|S_z = +1/2\rangle$ and $|S_z = -1/2\rangle$ are rather close to resonance. This is radically different from the case of strongly anisotropic molecular magnets (such as Mn_{12} or Fe_8) where the ground-state tunneling splitting is much smaller than hyperfine fields.

Finally, we consider the static dipolar interaction $\Gamma_0 \simeq 10^{-4}$ K between the molecules situated in the lowest four states (with $S = 1/2$). Longitudinal dipolar interactions (the terms $S_z^1 S_z^2$) are included in the mean field along with the static hyperfine field Γ_{hf} and can be neglected in comparison with the latter (since $\Gamma_0 \ll \Gamma_{hf}$). The terms $S_z^1 S_x^2$ etc. within the mean-field approximation change the tunneling splitting just negligibly (since $\Gamma_0 \ll \Delta_0$). But the flip-flop terms ($S_x^1 S_y^2$ etc.) cannot be incorporated into the mean-field scheme. Flip-flop between two molecules is a transition from the state $|S_z^1 = +1/2, S_z^2 = -1/2\rangle$ to the state $|S_z^1 = -1/2, S_z^2 = +1/2\rangle$. The matrix element of this transition is of order Γ_0, but the energy difference between the initial and final states is determined by the difference in local mean fields acting on the two molecules, which is of order $\Gamma_{hf} \gg \Gamma_0$. In this situation, known as Anderson localization, the levels of the molecule do not widen at all, and no spin diffusion is present. The localization can be lifted due to the dynamic change of the hyperfine field at the molecule, but this happens on a time scale $t \sim \tau_n$. At temperatures $T > 0.2$ K the coherence is already lost at these times, due to thermoactivated dipolar field fluctuations ($\Gamma\tau_n \gg 1$). At lower temperatures, the mean-field approach is not valid, and the intermolecular correlations should be taken into account.

Summarizing the discussion above, the dipolar dynamic fluctuations constitute an important source of decoherence at $0.2 < T < 0.5$ K. Let us formulate now a model for magnetic relaxation under the fluctuating dipolar field $\mathbf{h} = h_x\mathbf{e}_x + h_y\mathbf{e}_y + h_z\mathbf{e}_z$. We consider a two-level system (the levels $S_z = \pm 1/2$ for V_{15}) with the static tunneling splitting Δ_0 and static mean-field bias h_0 (the latter is governed mainly by the hyperfine static fields, since the demagnetizing fields are much weaker). The system is described by the density matrix ρ written in the basis formed by the levels $S_z = \pm 1/2$. Its equation of motion is

$$\dot\rho = i[\rho, \mathcal{H}], \tag{5}$$

where $\mathcal{H} = -(\Delta_0 + h_x)\sigma_x - h_y\sigma_y - (h_0 + h_z)\sigma_z$ is the Hamiltonian of the system ($\sigma_{x,y,z}$ are the Pauli's matrices). It can be conveniently written as

$$\begin{aligned} \dot x &= -h_y y - (\Delta_0 + h_x)z, \\ \dot y &= h_y x + (h_0 + h_z)z, \\ \dot z &= (\Delta_0 + h_x)x - (h_0 + h_z)y \end{aligned} \tag{6}$$

by introducing the variables: $x = (\rho_{11} - \rho_{22})/2$, $y = (\rho_{12} + \rho_{21})/2$, and $z = (\rho_{12} - \rho_{21})/(2i)$. The static fields Δ_0 and h_0 can be eliminated by two rotations of the coordinate frame:

$$\begin{aligned} x &= X\cos\varphi - (Y\cos Et + Z\sin Et)\sin\varphi, \\ y &= X\sin\varphi + (Y\cos Et + Z\sin Et)\cos\varphi, \\ z &= -Y\sin Et + Z\cos Et, \end{aligned} \tag{7}$$

where $\sin\varphi = \Delta_0/E$, $\cos\varphi = h_0/E$, $E = \sqrt{\Delta_0^2 + h_0^2}$, and Eqs. (6) take the form

$$\begin{aligned} \sqrt2\,\dot X &= (h_{2a} - h_{3b})Y - (h_{2b} + h_{3a})Z, \\ \sqrt2\,\dot Y &= \sqrt2\,h_1 Z + (h_{3b} - h_{2a})X, \\ \sqrt2\,\dot Z &= (h_{2b} + h_{3a})X - \sqrt2\,h_1 Y. \end{aligned} \tag{8}$$

The random fields acting on the system are $h_1 = h_z\cos\varphi + h_x\sin\varphi$, $h_{2a,3a} = \sqrt2\,h_{2,3}\sin Et$, and $h_{2b,3b} = \sqrt2\,h_{2,3}\cos Et$, where $h_2 = -h_z\sin\varphi + h_x\cos\varphi$ and $h_3 = h_y$. As we discussed above, $h_{x,y,z}$ are independent random fields, at any instant distributed with the same law (3); the same is true for $h_{1,2,3}$. Since $E\tau_c \geq \Delta_0\tau_c \gg 1$, one can consider $h_{2a,3a}$ and $h_{2b,3b}$ as independent, and in Eq. (8) we have several independent fluctuating fields with the same Cauchy distribution and with very short autocorrelation time τ_c.

Equations (8) can be imagined as describing the evolution of a system with the Hamiltonian $H = H_1 + H_2 + H_3$:

$$\dot{\mathbf{R}} = -iH\mathbf{R}, \tag{9}$$

where $\mathbf{R} = (X, Y, Z)$, $H_1 = \sqrt2(h_{2a} - h_{3b})S_1$, $H_2 = -\sqrt2(h_{2b} + h_{3a})S_2$, $H_3 = h_1 S_3$, and the noncommuting matrices $S_{1,2,3}$ are

$$S_1 = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \qquad S_2 = \begin{pmatrix} 0 & 0 & -i \\ 0 & 0 & 0 \\ i & 0 & 0 \end{pmatrix}, \qquad S_3 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix}. \tag{10}$$

The formal solution of Eqs. (9) can be represented in a path-integral-like form, by splitting the time interval $(0, t)$ into $N \gg 1$ equal pieces of length $\epsilon = t/N$:

$$\mathbf{R}(t) = \exp[-i\epsilon H(t_{N-1})]\cdots\exp[-i\epsilon H(0)]\mathbf{R}(0), \tag{11}$$

where $t_n = n\epsilon$. Each of the matrices H is proportional to the fluctuating fields $h_{1,2,3}$, so if we choose $\epsilon \ll \Gamma^{-1}$ the

Trotter decomposition formula [10] can be applied to each factor:

$$\exp\Big(-i\epsilon \sum H_k\Big) = \prod \exp(-i\epsilon H_k) + \mathcal{O}(\epsilon^2), \quad (12)$$

where $k = 1, 2, 3$. The correlation time of all the fields $h_{1,2,3}$ is τ_c, so $H_k(t)$ and $H_k(t + \epsilon)$ in Eq. (12) are decorrelated if $\epsilon \gg \tau_c$. Choosing $\tau_c \ll \epsilon \ll \Gamma^{-1}$, each term in the products (11) and (12) can be averaged independently over different realizations of the random processes represented by the fields $h_{1,2,3}$ thus giving the answer

$$\begin{aligned} \langle X(t)\rangle &= X(0)\exp(-2\sqrt{2}\,\Gamma t), \\ \langle Y(t)\rangle &= Y(0)\exp[-(\sqrt{2}+1)\Gamma t], \\ \langle Z(t)\rangle &= Z(0)\exp[-(\sqrt{2}+1)\Gamma t]. \end{aligned} \quad (13)$$

These results, together with Eq. (7), represent an exact solution of the problem. The situation considered here is similar to that found in spin resonance, and the results can be conveniently expressed in corresponding terms. The dynamics of the density matrix elements is represented as a sum of two terms: damped oscillations with the frequency E [with transverse relaxation rate $T_2^{-1} = (\sqrt{2}+1)\Gamma$] and pure damping (with longitudinal damping rate $T_1^{-1} = 2\sqrt{2}\,\Gamma$). The decoherence times $T_{1,2}$ both are of order Γ^{-1}. This holds in spite of the smallness of τ_c, due to the peculiar properties of the Cauchy distribution: for Gaussian fluctuations with variance σ^2 we would have much smaller relaxation rate $\sigma^2\tau_c$ (motional narrowing [8]). On the other hand, if τ_c were very large then the dipolar field would be almost static, and the decoherence time for a single molecule would be determined by hyperfine fields, as it is for Mn_{12} or Fe_8 [7].

Nevertheless, for V_{15} the decoherence rate is still small enough: $\Gamma/\Delta_0 \simeq 2 \times 10^{-7}$ at $T = 0.5$ K, i.e., the system tunnels about 5 000 000 times before the tunneling oscillations are wiped out by decoherence. We emphasize that each tunneling in V_{15} is *not* a single-spin event: it takes place between the two states of the whole molecule. It is a tunneling of an antiferromagnetic system with small uncompensated spin, and *all* 15 spins are involved.

Summarizing, we considered possible sources of decoherence in V_{15} molecules between the states $S_z = \pm 1/2$ of ground-state doublets. We found that in the temperature region 0.2–0.5 K the main source of decoherence is the fluctuating dipolar field created by the molecules, which are thermally activated to the higher $S = 3/2$ level. Based on an exactly solvable model, a rather low decoherence rate is found: about 5 000 000 tunneling events occur before the coherence is destroyed. Such a low decoherence rate is unusual for magnetic systems of mesoscopic size at these temperatures.

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